

Precipitation Effect on Mg^{2+} Ions Sorption by $FePO_4$

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Summary: Potentiometric titrations of $FePO_4$ in the presence of Mg^{2+} were carried out under different experimental conditions. The precipitation of Mg^{2+} ions in the absence of $FePO_4$ was measured potentiometrically as a function of concentration, pH and temperature. The shift of the titration curves at a given temperature in the presence of exchanger ($FePO_4$) is related to the metal ions adsorption at pH values below the plateau formation in the titration curves. It was found that the process of uptake of the Mg^{2+} changes from adsorption to precipitation with the increase in concentration, pH and temperature.

Introduction

Ion exchange sorption is an important process for the removal of heavy metals from an aquatic environment which is in contact with the soil or the suspended solids. Sorption processes include some solute accumulation processes onto a solid surface such as adsorption, ion exchange, precipitation, co-precipitation and polymerization [1]. These processes often act together, and the dominance of one specific process over the others is often hard to distinguish without careful chemical measurements and advanced analytical techniques. The ion exchange sorption of metal cations on various exchangers has been undertaken in great detail [1-5]. We have also reported in detail about the sorption properties of some new ion exchange materials such as $AlPO_4$ [6, 7], $CrPO_4$ [8] and $FePO_4$ [9, 10]. However, no detailed study has been reported on these adsorbents regarding their precipitation [11] effect on the adsorption process of metal ions. During the present investigation an attempt has been made to evaluate potentiometrically the effect of precipitation on the ion exchange sorption of Mg^{2+} by $FePO_4$ particles. The study is significant as it may provide an insight in understanding the interaction of the Mg^{2+} with the naturally occurring $FePO_4$ i.e. strengite.

Results and Discussion

Characterization of $FePO_4$

The surface area of the $FePO_4$ was found to be $60 \pm 1 \text{ m}^2/\text{g}$ and the X-ray diffraction showed that the sample is amorphous in nature. The wet chemical analysis gave a value of 1.09 for Fe/P molar ratio, which is close to the ideal value of 1.00. The thermal analysis of the sample indicated that the formula of the solid was $FePO_4 \cdot 2H_2O$ as on the average 2 moles

of water molecules were lost when the solid was heated to $600 \pm 5^\circ\text{C}$.

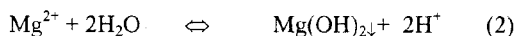
Potentiometric Titration Studies of the $FePO_4$

The potentiometric titration curves of $FePO_4$ in the presence of Mg^{2+} ions are given in Figs. 1 and 2. Fig. 1 shows that the divalent Mg^{2+} ions shift the curves towards lower pH values as compared to the alkali metal K^+ ions. This shift in the curves of Figs. 1 and 2 increases with the increase in temperature of the system, and indicates that the sorption of the divalent metal cations is accompanied by greater release of the H^+ ions from the exchanger into the suspension. The shift in the titration curves towards the low pH values in the presence of divalent metal cations is also indicative of the release of protons from the solid surface by the sorbed metal cations [6-11] and hydrolysis/precipitation of the metal cations which are involved in the liberation of protons. As such, the decrease in the pH of the aqueous suspension may be represented by the following possible mechanisms:

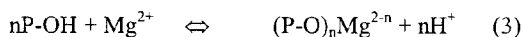
Hydrolysis of Mg^{2+}



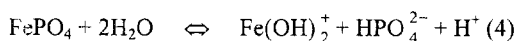
Precipitation of the Mg^{2+}



Cation exchange reaction



Hydrolysis of the $FePO_4$



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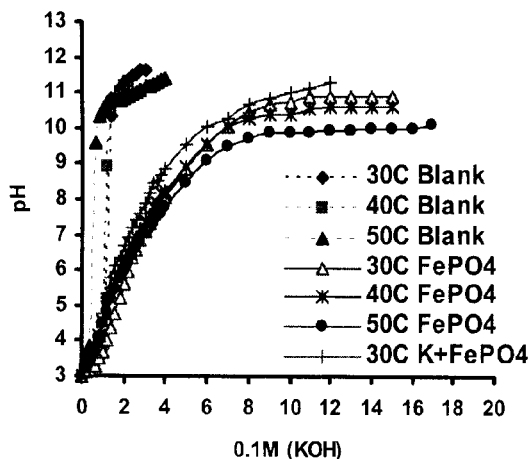


Fig.1: Potentiometric titration curves of FePO_4 in the presence of 20 ppm Mg^{2+} at different temperatures. (dotted lines represent the titration curves of Mg^{2+} in the absence of FePO_4).

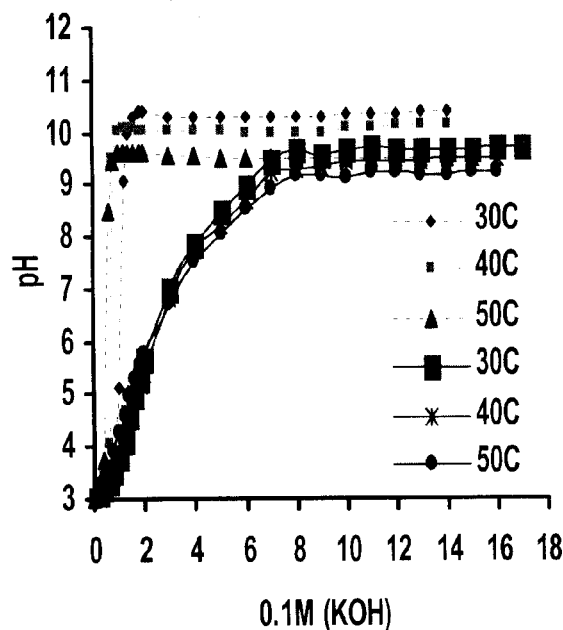


Fig.2: Potentiometric titration curves of FePO_4 in the presence of 500 ppm Mg^{2+} at different temperatures. (dotted lines represent the titration curves of Mg^{2+} in the absence of FePO_4).

The exchanger, FePO_4 , was observed to be hydrolytically stable as its dissolution was found to be almost negligible under the given experimental

conditions [7, 8]. Thus, the possibility of reaction (4) may be ruled out and the release of protons may be attributed either to the hydrolysis/precipitation (reactions 1 and 2) or to the cation exchange process (reaction 3).

To distinguish between the ion exchange sorption and the precipitation of metal ions, blank titration curves of Mg^{2+} (without FePO_4) along with 0.1M KCl are also presented in Figs. 1 and 2. It can be seen from these curves that a marked shift in the presence of FePO_4 occurred towards lower pH values in comparison with the blank titration curves of the divalent metal cations. The protons responsible for the ion exchange reaction can be calculated from the difference between the blank run and each curve of the Mg^{2+} ions in the presence of the FePO_4 . The ratio of the excess amount of the base consumed in the presence of the FePO_4 gives the concentration of the surface protons responsible for the sorption of metal cations [7, 10, 11]. The shape of the curves (Figs. 3, 4) demonstrates that precipitation effect is negligible for lower concentrations of the metal cation at high pH and temperature, showing that the H^+ ions are released from the FePO_4 into the aqueous phase according to reaction (3). However, the effect of precipitation becomes pronounced only when concentration of the divalent metal cations in solution is increased beyond a certain limit (Figs. 3, 4). These results suggest that at high concentration of Mg^{2+} ions the sorption process is replaced by precipitation. The curves given in Figs. 1 and 2 also demonstrate that the temperature plays an important role in precipitation of the Mg^{2+} ions. Moreover, the plateau

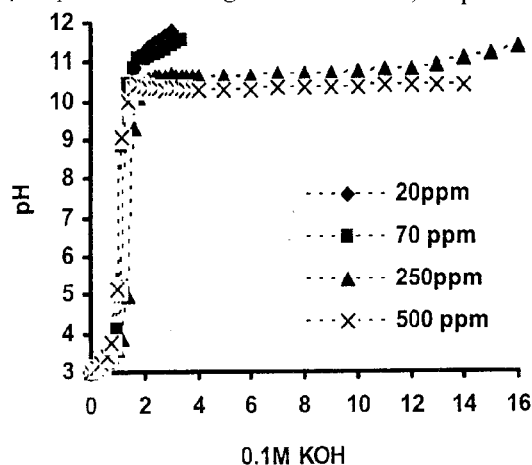


Fig.3: Potentiometric titration curves of different concentrations of Mg^{2+} only at 303K.

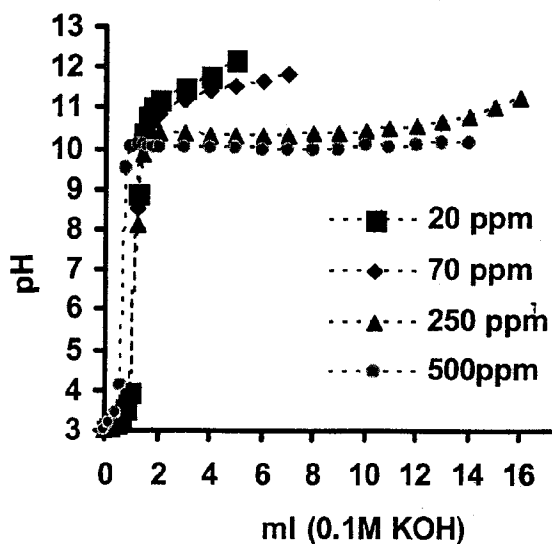


Fig.4: Potentiometric titration curves of different concentrations of Mg^{2+} only at 313K.

formation takes place at lower pH values at higher temperatures, confirming that at higher temperatures the precipitation of metal cations is favored.

Experimental

$FePO_4$ as desired elsewhere [8] prepared in the laboratory was well characterized. All solutions were made with ACS grade chemicals and doubly distilled deionized water.

Potentiometric Titrations of $FePO_4$

Sixty milliliters (ml) of Mg^{2+} ions of different concentrations (20 – 500 ppm) along with the background electrolyte (0.1M KCl) containing 0.2 g solid sample were taken in a thermostated double-walled pyrex cell. The suspension was initially equilibrated for 30 minutes with constant stirring by using a magnetic stirrer at the desired temperatures (303, 313 and 323 K). After equilibration, pH of the suspension was measured with pH meter model Orion Sa 520. The standardized solution of potassium hydroxide was added by means of microburette with

intervals of 0.2 ml. After each addition of the base, suspension was further equilibrated for 2 minutes with constant stirring, at the end of which the changes were less than 0.01 pH units/minute. The blank titrations were performed under similar conditions of pH, temperature and concentration of the metal cations in aqueous solutions. The only difference in the experimental procedure was that in case of a blank titration, no $FePO_4$ was present in the solutions of Mg^{2+} cations.

Conclusions

From the potentiometric titration data, it can be summarized that ion exchange sorption is more favorable process for the uptake of Mg^{2+} by $FePO_4$ at low concentration, temperature and pH, which changes into precipitation with the increase in concentration, temperature and pH of the aqueous solution.

References

1. K. Dorfner, Ion Exchangers, Walter de Gruyter Berlin, New York (1991).
2. W. Stumm, and J.J. Morgan, Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters, Ed.2nd, John Wiley and Sons, New York, p. 283 (1981).
3. J. Perrone, B. Fourest, and E. Giffaut, *J. Colloid Interface Sci.* **239**, 303 (2001).
4. A. Clearfield, Inorganic Ion Exchange Materials, CRC Press Boca Raton FL, (1982).
5. P. Schaad, F. Poumier, G.C. Voegel and P. Gramain, *Colloids Surf.* **121**, 217 (1997).
6. S. Mustafa, A. Naeem, and N. Rehana, *J. Chem. Soc. Faraday Trans.* **89**, 3843 (1993).
7. A. Naeem, S. Mustafa and N. Rehana, *J. Colloid Interface Sci.*, **252**, 6 (2002).
8. S. Mustafa, A. Naeem, and N. Rehana, *J. Colloid Interface Sci.*, **220**, 63 (1999).
9. A. Naeem, S. Mustafa, and N. Rehana, *Environmental Technol.*, **23**, 583 (2003).
10. S. Mustafa, A. Naeem, and N. Rehana, *Adsorption Sci Technol.*, **19**, 701 (2001).
11. A. Naeem, S. Mustafa, B. Dilara and N. Rehana, *J. Chem. Soc. Pak.*, **25**, 98 (2003).